

Relationships between micro-fibrillar angle, mechanical properties and biochemical composition of flax fibers

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Abstract

An elementary plant fiber could be assimilated to a laminate, mainly constituted of the secondary wall S2 layer, made of a few non-crystalline polysaccharides reinforced by cellulose fibrils organized in a helix, with a microfibrillar angle (MFA) around 10° relative to the longitudinal fiber axis. This paper investigates the relationships between the MFA, the mechanical properties and the biochemical composition of different varieties of flax. To conduct this study, tensile tests on elementary flax fibers, X-ray diffraction, and solvent extractions have been carried out. Within the different varieties of flax, Young's modulus was found to be negatively correlated with the MFA. The results showed that the ratio between hemicelluloses (matter extracted with alkali) and pectins (hydrolyzed with acids) is highly correlated with the tensile properties; concurrently, we showed the great influence of pectic acids on the fiber's Young's modulus, and on the orientation of the microfibrils.

Key words:

Flax fiber; mechanical properties; biochemical composition; micro-fibrillar angle; X-ray diffraction

1 Introduction

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2 The depletion of our natural resources, as well as the increasing impacts of our society on
3 our environment, suggest that there is a need for new research in the design of composite
4 materials. Thus, for many industrial products, plant fibers could be used as a substitute
5 for synthetic fibers in composite materials reinforcement. In Europe, the most interesting
6 are flax and hemp fibers, due to their high-performance specific mechanical properties
7 (Bourmaud and Baley, 2009), their environmental and ecological benefits (Le Duigou et
8 al., 2011), as well as their low cost.

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10 Flax or hemp fibers exhibit a complex, hierarchical and multi-component structure; they could
11 be considered, at their scale, as complex composite materials. Figure 1.a (Hearle, 1963)
12 presents the general structure of a flax fiber.

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14 Flax fibers commonly have a polygonal section, and are arranged into concentric cell-wall layers
15 with a channel in the middle, called the lumen, which corresponds to the remains of the
16 cytoplasm and nucleus. As a sink, it may play a major role in the water sorption of the material
17 (Alix et al., 2009b). The outer cell wall is called the primary cell wall, it is around 200 nm thick
18 (Gorshkova et al., 1996; Roland et al., 1995); this wall has a structural role by ensuring the fiber
19 length continuity and is made of pectins, poorly crystallized cellulose, and xyloglucans as the
20 main hemicelluloses moieties (Gorshkova et al., 1996). The bulk of the fiber cell walls is
21 constituted by the secondary wall, and is divided into 3 different layers - S1 (0.5-2 μm thick), S2
22 (5-10 μm) and S3 (0.5-1 μm)- and provides the reinforcement of the plant structure. The average
23 diameter of a flax fiber is around 15 μm (Pillin et al., 2011). The main layer, representing around
24 80% of the total section, is the S2 layer, constituted of highly crystalline cellulose fibrils spirally
25 wound in a matrix of amorphous hemicelluloses and pectins (Goubet et al., 1995); the cellulose
26 fibrils make a 10° angle with the axis of the fiber (Bledzki and Gassan, 1999)- which is called
27 micro-fibrillar angle (MFA)- and their crystallinity is about 65% for the secondary cell wall fibrils
28 (Kalia and Kaith, 2008). The geometrical characteristics of these fibrils could vary depending on
29 authors; Whistler et Richards (Whistler and Richards, 1970) found a diameter between 10 and
30 30 nm. Based on X-ray diffraction measurements, Muller et al. (Muller et al., 1998) studied
31 elementary fibers extracted from flax fibers. They showed the non periodicity of the micro-fibrils
32 arrangements along the fiber and they estimated the cellulose fibrils diameters between 2 and 3
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nm. These different values point out the different levels of geometrical structures i.e. either pure cellulose microfibrils whose geometry entirely depends on the organization of cellulose-synthase complex in the cell-plasmalemma, or macro-fibrils coated with hemicelluloses that contained a certain number of non-coated microfibrils.

Due to this multi-component structure, plant fibers have a complex mechanical behavior (Baley, 2002); figure 1.b shows a typical stress-strain curve of flax fiber. After a first zone corresponding to the beginning of the fiber loading, we can distinguish a non-linear part probably induced by the initiation of the reorientation of cellulose fibrils in the secondary wall (S2). Thus, Burgert (Burgert, 2006) evidenced that a decrease in the MFA was associated with an improvement of the tensile strength on wood fibers. As assumed by Baley (Baley, 2002), the non-linearity that is noticed at the beginning of a stress-strain tensile curve may be associated to the realignment of cellulose micro-fibrils. Some recent works corroborated this hypothesis by pointing out that the micro-fibrillar realignment during a tensile loading was not complete for hemp (Placet et al., 2011) or flax (Thuault, 2011).

According to Hearle (Hearle, 1963), this reorientation is caused by the shearing of the polysaccharide network during the loading; this loading induces an increase in the cellulose fibrils' length as well as in the inter-fibrillar amorphous areas. The second region of the loading curve appears linear, a typical characteristic for an elastic behavior. At this particular moment, the cellulose fibrils are probably more aligned in the direction of the tensile axis.

Plant fibers generally exhibit an important spread of their mechanical properties. Various intrinsic or exogenous parameters could influence these mechanical properties. The main object of our study is to focus particularly on intrinsic parameters such as micro structural conformation, cellulose fibril orientation, and biochemical composition.

In flax cell walls, the cellulose macro fibrils are embedded in an amorphous polysaccharide matrix composed mainly of pectins and hemicelluloses. The hemicelluloses not only act as a matrix but also, thanks to a structure similar to that of cellulose, may act as a coupling agent (Baley, 2002; Morvan et al., 2003); its nature varies according to whether it is in the primary layer of fibers (e.g. xyloglucan) or in the secondary layer (xylanes and glucomananes). Alix et al. (Alix et al., 2009b) compared the structure and the mechanical properties of oleaginous (Oliver) and textile (Hermes) flax. They evidenced higher mechanical performances for the

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Hermes flax (Young's modulus of 68 ± 36 GPa for Hermes, and 38 ± 13 GPa for Oliver; tensile strength of 1450 ± 840 MPa for Hermes, and 720 ± 290 MPa for Oliver), correlated to the cellulose contents of the two varieties ($84 \pm 3,5$ % for Hermes, and $77 \pm 2,5$ % for Oliver). They explained this phenomenon by the inter-fibrillar distances (lower for Hermes) due to lower amount of non-cellulosic polymer matrix between these cellulose fibrils. In the case of Hermes flax, the presence of glucomannan bridges could explain part of the stiffness differences.

Due to its important Young's modulus, around 135 GPa (Kroon-Batenburg et al., 1986), the cellulose content mainly influences the mechanical properties of plant fibers, as evidenced by Alix et al. (Alix et al., 2009a); the poor mechanical properties of the other constituents- some works on wood showed a stiffness of 2 GPa for the hemicelluloses (Salmén, 2004) in dry atmosphere (12%), and 20 MPa in moist conditions- results in a small negative impact. In general, in plant fibers, the higher the cellulose rate the better the mechanical properties; we can quote the example of flax (Baley, 2002) which has an important cellulose content and very interesting mechanical properties. Nevertheless, the cellulose content is not the only influential parameter; a good counter-example is given by cotton, which has a very important cellulose content (between 82 and 99%) and exhibits poor mechanical properties (John et al., 2008).

As underlined before in this paper, the micro-fibrillar angle (MFA) has an important influence on the mechanical behavior of plant fibers, and it could be considered as an important structural parameter. This MFA could differ according to the species under study. Thus, Salmén (Salmén, 2004) compared the MFA values of various wood fibers with their associated mechanical properties. This work highlighted important rigidity differences according to the measured MFA. This discrepancy is present among plant fibers. The MFA of flax or hemp fibers, which exhibit high mechanical properties, ranges from 8 to 11° (Bledzki and Gassan, 1999; Placet et al., 2011) whereas sisal, which has an important MFA (around 20°), exhibits modest mechanical properties (Idicula et al., 2005). The MFA could be approached through microscopic methods (Scanning Electronic Microscopy (SEM) or Atomic Force Microscopy (AFM) but, due to the low dimensions of the studied areas, it is very difficult to obtain an absolute MFA value, at the scale of the fiber. A few research teams have used X-ray diffraction to understand the influence of the MFA on the mechanical properties of plant fibers or wood (Burgert, 2006). The first X-ray investigations on plant fibers are attributed to Meyer (Meyer and Lotmar, 1936) on ramie; they

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calculated the crystalline modulus of the cellulose under loading from the 040 diffraction plane. Other authors (Mann and Roldan-Gonzalez, 1962; Young and Eichhorn, 2007) confirmed these results. Cave (Cave, 1997) showed, as far as wood is concerned, that the intensity profiles of 040 planes make it possible to obtain a direct measure of the MFA distribution into the S2 layer. The purpose of this work is to contribute to the knowledge of the impact of the plant fibers micro-structure, and the biochemical composition on their mechanical properties. We selected various oleaginous and textile flax fiber varieties representing a range of mechanical behaviors. First, we determined the fibers' MFA by using X-ray diffraction before investigating their biochemical composition. The paper closes on a discussion about the interactions and correlations between the mechanical, structural and biochemical results.

2 Experiment

2.1 Flax fiber

Table 1 shows the different flax varieties used for this study.

Five oleaginous flax fibers (two Everest, E5 & E8, Alaska, Hivernal and Oliver) were provided by the "Chambre d'Agriculture du Morbihan" (Chamber of Agriculture of Morbihan in Brittany, France). They were grown in the same geographic area over a four year period (2005 to 2008). These flax plants have been cultivated on the same geographic area and lands in a temperate region (West of France). These varieties were sowed in October and harvested during the winter months, in opposition to the spring culture, which is common practice for textile flax. As seen by the seed yield it is likely that the Everest culture of 2005 (named E5) was pulled at lower maturity than the Everest culture of 2008 (named E8) (Pillin et al., 2011). The Hermes, Agatha and Ariane textile flax were harvested in the North-West of France, in Normandy, at the beginning of September, being sowed in the beginning of April, and pulled in August. After being pulled, plants were laid over the field for 4 weeks to allow stem drying and dew-retting. Retting consists in the development of fungi within the stems, which degrades their cortical tissues, and further facilitates the extraction of the fibers. The retted plants were further

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scutched to extract what we designated as technical fibers, which consisted of a partially divided bundle (diameter range 60-80 μm) containing 15 or more elementary fibers.

All the selected fibers were manually extracted from the middle of the stem.

2.2 Tensile tests on elementary flax fibers

Tensile tests on single fibers were performed. Fiber samples were stocked in a controlled environment (temperature of 23 \pm 0.5°C, and relative humidity of 48 \pm 1%) during at least 2 weeks, and longitudinal mechanical properties (Young's modulus, ultimate strength and failure strain) were determined in the same environment. Due to the short fiber length (about 20–30 mm), a gauge length of 10 mm was chosen. The fiber was clamped on a universal MTS type tensile testing machine equipped with a 2 N capacity load cell and loaded at a constant crosshead displacement rate of 1 mm/min up to rupture. The determination of the mechanical properties was made in accordance with the NFT 25-704 standard which takes into account the compliance of the loading frame. For each type of fibers, at least 50 fibers were tested. Before the tensile test, the diameter of every fiber was measured with an optical microscope. The diameter taken into account is an average value from five points obtained along the fiber. Only fibers exhibiting a constant diameter were used for the tensile tests.

As shown in figure 1.b, the stress-strain curve of flax fibers shows a non-linear region in the early stage of loading. Such a behavior may be partly explained by the sliding of the micro-fibrils along with their progressive alignment with the fiber axis, as can be noticed for flax fibers (Baley, 2002). The second region of the loading curve appears linear, this region being characteristic of an elastic behavior. The Young's modulus of the fiber is evaluated through the slope of the curve in this region.

2.3 Estimation of flax fiber micro-fibrillar angles by X-ray diffraction

An X-ray diffractometer from Oxford diffraction (Supernova model) was used to estimate the micro-fibril angle. The Supernova system consists of:

- A kappa geometry, four circle goniometry for sample orientation with a detector arm.
- A CCD area detector delivering a digitized signal to 18-bit resolution.
- An X-ray tube, with a copper source, the nominal point of which is at 50 keV/1 mA.

1 The X-ray optics consists of a high speed shutter located next to the tube shield, a
2 monochromator that can select the $K\alpha$ peak and a collimator designed to limit the beam
3 divergence. At the sample position, the beam diameter is about 300 μm . The sample can be
4 observed with a video microscope for accurate positioning. The operating temperature of the
5 CCD is -40°C . In these conditions, the dark current is less than 0.2 electrons per pixel and per
6 second, and a dark noise subtraction needs to be systematically done. This makes it possible to
7 keep a good signal/noise ratio with a fiber bundle of about 100 μm in diameter.

8 In this device, the four-circle goniometry allows for a really accurate positioning of the sample in
9 the X-ray beam, thereby making the measurement on a single fiber bundle possible.

10 In order to estimate the micro-fibril angle for elementary flax fiber bundle, a five-step
11 methodology is used:

12 *Step 1: Calibration*

13 The beam center is determined from the figure obtained when using crystal powder. A 300 μm
14 diameter capillary is filled with silicon powder, and exposed to X-rays for 60 s. As expected, the
15 diffraction pattern depicts light spots situated over a perfect circle. The coordinates of its center
16 are determined thanks to an inverse method that uses the Nedler Mead algorithm. The
17 parameters to be estimated are the center coordinates and the circle radius with an objective
18 function based on the averaged intensity level over the circle.

19 *Step 2: Estimation of the 002 optimal circle*

20 On a diffraction pattern, the optimal circle, in the sense of the maximal mean intensity is
21 determined by using the Nedler Mead algorithm with the previously determined center
22 coordinates (Step 1), and one single free parameter which is the circle radius (Fig. 2.a). The
23 objective function is defined as follow:

$$24 f(r) = \frac{\int_0^{2\pi} \int_{r-\Delta r}^{r+\Delta r} I(r, \theta) r d\theta dr}{4\pi r \Delta r}$$

where r is the identified radius originated from the center that was identified in step 2, and Δr is a radius gap (of some pixels) that is required in order to apply the previous equation in the case of discrete positions.

Step 4: Extracting the diffraction pattern

In order to smooth the angular intensity profile, the intensity at each angle θ of the optimal circle (Step 3) is determined from an average over the pixels located in a region of interest (ROI) surrounding the location. Such a ROI is defined by an angle range $\theta \pm d\theta$ and a radius range $r \pm dr$. The ROI has to be large enough for the curve to be smooth, and small enough for the diffraction curve to remain unaffected. In this work, we used standard parameters 0.1° for $d\theta$ and 25 pixels for dr (with $dr/r \approx 0.1$).

Step 5: Micro fibril identification

The MFA is estimated through curve fitting, using a Nelder-Mead least square routine. The objective function evaluates, in the sense of the squared residues, the difference between the experimental profile and a theoretical function, which includes two Gaussian curves and a baseline:

$$y = A_0 + A_1 \exp\left(-\frac{(x - m_1)^2}{\sigma_1}\right) + A_2 \exp\left(-\frac{(x - m_2)^2}{\sigma_2}\right)$$

The MFA is then deduced from the parameters of the fitted function according to Cave's equation (Cave, 1997):

$$MFA = 0.6T$$

With $T = \sigma_1 + \sigma_2$. The MFA identification is illustrated in Figure 2.b.

This linear relationship between MFA and the width of the diffraction peak was calibrated by optical methods performed on the same set of samples. This factor is used in routine determination, but we have to keep in mind that the curve shape depends on the mean angle, its standard deviation and the shape of the cellular structure. Even though more sophisticated methods are proposed to extract the angle distribution, this widely-used method remains a good

1 way to evaluate the mean microfibril angle, namely to compare the value of MFA within a same
2 species.

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4 The entire methodology was applied in this work for the estimation of the micro-fibril angle of
5 several flax varieties. For each variety, ten samples were submitted to X-ray diffraction. For
6 each fiber, several acquisitions were performed along the longitudinal axis, as illustrated in
7 Figure 2.c. The exposure time was set to 60 seconds in order to get the optimal ratio signal/
8 noise. Four images of 60 seconds were used for the dark noise subtraction. A 2 by 2 binning
9 produces a 1024 by 1024 resolution. The results will be presented and discussed in section 3.
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19 2.4 Extraction of polysaccharides and sugar analysis

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21 Retted fibers consisted of more and less divided bundles whose surface features areas are
22 contaminated with cortical debris that are rich in pectins (referred to as surface pectins), and
23 could be partly eliminated with boiling water (Morvan et al., 1990). Besides, pectins from fiber
24 junctions could be extracted with boiling EDTA (Goubet et al., 1995). Thus, in order to divide the
25 bundles into elementary fibers, these technical fibers were pre-treated at 100°C (3 x 2h) with
26 water, and then with EDTA-Na₂. On the whole, 13.0 ± 0.5% to 20 ± 2% of dry matter was
27 removed from the technical fibers of, respectively fiber flax and oleaginous varieties. The
28 difference between the two types of flax is mainly originated from the largest stem section of the
29 oleaginous varieties with large amount of cortical tissues to be degraded.
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39 The cleaned fibers were then successively treated with 0.02 M HCl and 1.5 M NaOH/ 100mM
40 NaBH₄ (once 1h 100°C+ twice in H₂O for 1h at 100°C) in order to release the polysaccharides
41 (named EH and EOH, respectively) that encrusted (EH) and coated (EOH) the cellulose
42 macrofibrils (Charlet et al., 2007). Although EOH might contain pectic polymers (Alix et al.,
43 2009b), they were sometimes referred to as hemicelluloses, because of the alkali treatment.
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50 Three independent series were run for each sample. Total sugars and galacturonic acids were
51 colorimetrically assayed (Blumenkrantz and Asboe-Hansen, 1973; Dubois et al., 1956).
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3 Results and discussion

3.1 Impact of the flax variety on the mechanical properties of flax fibers

Table 2 reports the Young's modulus, strength and elongation at break of the flax fiber samples studied. Most varieties had been studied by our research team in previous works (Baley, 2002; Charlet et al., 2007; Charlet et al., 2009; Pillin et al., 2011). The Oliver variety has been characterized during this work. In addition to these flax fibers, the mechanical properties of hemp fibers (Placet, 2009) are indicated.

The tensile values were characterized by a broad distribution; however we have to keep in mind that plant fibers are natural products which do not have, in essence, repeatable properties and which exhibit many defaults, particularly after elementary fiber extraction. The data spread could be due to approximations of the geometrical characteristics necessary to calculate tensile modulus and strength. Among other approximations, we consider an average diameter for the whole fiber even if the cross-section is smaller near the end. The influence of this approximation has been studied in previous works (Baley and Lamy, 2000; Lamy and Baley, 2000). Moreover, the mechanical properties spreading could be due to outside parameters like inconstant growing fibers conditions (temperature, hygrometry, sunshine time or soil quality). These growing conditions can be subjected to many variations during fiber development. The fibers collecting area into the plant could be an important factor as evidenced by Charlet et al. (Charlet et al., 2007) and the presence of pectin on fibers could prevent one from being able to measure the resistant section.

First, we can notice some important mechanical properties variations between the different flax fibers. In general, the average values of Young's Modulus, stress and strain at break of the textile-type varieties were higher (although not significantly so) than oleaginous-type varieties. For two varieties of the same type, cultivated the same year in the same geographic area, therefore probably submitted to the same climatic conditions, important mechanical property differences can be noticed. This is especially the case for Alaska and Hivernal 2006, cultivated in the same geographical area. These observations indicate that the genetic pool of each type and variety probably has some influence on their mechanical properties. Moreover, a local analysis of the soil composition and of the parcel orientation could yield interesting informations. Altogether, the lowest tensile properties were typical of some varieties of the oleaginous type,

1 but the high values of Everest 2008 and Hivernal 2006 showed the possibility of high values for
2 the oleaginous type. We might hypothesize that oleaginous type fibers were more sensitive to
3 the impact of bad growth conditions.
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5 The important parameters are exogenous factors such as pedoclimatic conditions (temperature,
6 hygrometry, and sunshine time or soil quality). From one year to the next, opposite weather
7 conditions can be observed, which could induce important mechanical property gaps, as
8 evidenced with the Everest 2005 (E5) and 2008 (E8) varieties. Some particular weather
9 conditions (severe drought, for example) could induce hydric stress, which can be prejudicial to
10 the development and the maturation of flax fibers. In addition, the harvesting time could be an
11 important parameter. In the case of Everest, recent works (Pillin et al., 2011) showed that the
12 2005 variety (E5) has a slightly higher average diameter than those of the other culture years.
13 This result seems to be correlated with very low yields of seed obtained in 2005 which, as noted
14 above, indicated that the maturity of E5 was lower than that of E8. The high average diameters
15 might be related to the lack of fiber structuring which occurred during the last step of seed
16 maturation (Morvan et al., 2003); generally, mechanical properties and average diameter are
17 correlated and higher mechanical properties are found for lower diameters (Baley, 2002).
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32 Whatever the endogenous or exogenous impacts on mechanical properties, it would be
33 worthwhile to approach these differences in terms of cell wall structure - which means chemical
34 composition (Alix et al., 2009a) - but also micro-fibril cristallinity and arrangement.
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38 In the second part of this experimental section, we focus on the determination of the MFA fibers
39 by using X-ray diffraction.
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45 3.2 Use of the X-ray diffraction to estimate the flax fiber MFA

46 Table 3 reports the MFA of the different flax varieties under study. They were obtained by using
47 X-ray diffraction.
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51 The MFA values ranged between 8.3 and 9.5° according to the variety of flax fiber. The
52 standard deviations - from 1.1 to 4.3% - are acceptable. The micro-fibrillar values that were
53 obtained correlate well with those of the literature. There are few papers about direct
54 experiments on flax fibers; Astley et al. (Astley and Donald, 2001), by using X-ray diffraction
55 obtained MFA around 15° for wet flax fibers and 11° for the dry same fibers ; by using an
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1 alternative method, Muller et al. (Muller et al., 1998) studied the flax fiber morphology by X-ray
2 diffraction on bundles and not elementary fibers. The MFA they report is around 3.5°. The
3 authors explained this low value by an inappropriate fiber presentation (as bundles), or by the
4 existence of an additional signal arising from refraction effects at the fiber edge.
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7 These low angles differ from the literature's conventional values. Some authors report MFA
8 values around 10° for flax fibers (Bledzki and Gassan, 1999), which is well correlated with our
9 results. However, our MFA results have to be tempered due to the scale measurement. The
10 XRD apparatus does not make it possible to estimate orientation on an elementary cell; it could
11 be interesting, in forthcoming work, to carry out new experiments, at low scale, in order to obtain
12 information at the cell wall scale. These investigations could be performed on a Synchrotron
13 machine, which exhibits a very low spot size suitable for elementary fibers.
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25 3.3 Biochemical composition of the flax studied varieties

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27 After being cleaned in boiling water and EDTA, seven fiber samples (Ariane, Agatha, Hermes,
28 Everest 2005 and 2008, Hivernal and Oliver) were submitted to acid and basic extractions, and
29 the corresponding extracts EH and EOH were collected. The cellulosic residue (RC)
30 corresponds to the remaining fiber amount after acid and basic extractions. After this first
31 cleaning step, the galacturonic acids (UA) that were present in the EH and EOH solutions were
32 colorimetrically assayed.
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35 Table 4 presents the cell wall composition of the flax fibers, and figure 3 shows the EH and
36 EOH fractions as well as the cellulosic residue (RC), remaining after acid and basic extractions.
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39 First, we can notice that the sum of EH and EOH relative percentages were higher in
40 oleaginous (19.9 ± 1.8) than in textile (15.4 ± 1.0) varieties, (Figure 3). Conversely, the cellulosic
41 residue (RC) was higher in textile flax than in oleaginous varieties. As shown in the simplified
42 figure 4, EH moieties would correspond to the secondary wall pectins, while EOH matter mainly
43 represented hemicelluloses, coating with the micro-fibrils, and showing various conformations.
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45 As reported cell wall models (Cosgrove, 2005; Jarvis, 2009) they could be linearly arranged
46 along the micro-fibrils, or form bridges, loops or free chains, inducing main differences into the
47 cell wall stiffness. As indicated by Alix et al. (Alix et al., 2009b), EOH also contained structural
48 pectins ensuring some kind of interphase between the cellulosic micro fibrils and the matrix
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pectins (EH). Thus, oleaginous Oliver and textile Hermes flaxes were shown to exhibit important differences in their cell wall positions or structures, mainly in the amount of EH and ratio of pectic acid between EOH and EH.

Secondly, when the galacturonic acids (UA) were expressed in mg per mg of extract (UA EH¹ & UA EOH¹), the values in the textile-type fibers were slightly higher than in oleaginous-type ones, i.e. 0.14 ± 0.01 / 0.10 ± 0.01 in EH, and 0.073 ± 0.005 / 0.061 ± 0.004 in EOH. On the other hand, when expressed per 1g of pre-treated fiber (UA' EH² & UA' EOH²), the average values were similar in both type of flax, due to the largest amount of extracted matter in oleaginous type. These UA in EH were mainly associated to S2 cell wall matrix pectins whereas those present in EOH corresponded to more structural pectins. The ratio UA' EOH/OH³ quantifies the relative content of structural pectins. The average values were similar in both types of flax. When taken together, the number of micro mol of UA per g of fibers accounted for 77 ± 3, which is characteristic of well retted fibers.

3.4 Discussion and interpretations

Table 5 shows the correlations between the biochemical composition and the MFA values with the mechanical properties obtained on elementary flax fibers. The coefficient of determination r² values are calculated considering the hypothesis of a linear relationship. The (-) sign corresponds to a negative slope.

First, a negative correlation can be noticed between EH and the stress at break (r²= -0.52), on the one hand, and with the strain at break (r²=+0.56), on the other hand. The more important the EH quantity, the larger is the inter-fibrillar space absorbing the tensile stress, which allowed for more sliding between macro-fibrils. Due to its moderate variability, EOH isn't correlated with the mechanical parameters. Possibly, it is negatively related with MFA: the higher the EOH, the lower the MFA. The EOH/EH ratio is positively related to all the tensile parameters. This result confirms the importance of the EOH/EH ratio which conditions the mechanical performances of the cell walls, which as was previously hypothesized by Alix et al (Alix et al., 2009a) when studying only two varieties.

The percentage of cellulosic residue was not correlated with the strength and Young's modulus, but was slightly so with the strain at break. Moreover, due to the great mechanical properties of

1 the cellulose (around 135 GPa) (Kroon-Batenburg et al., 1986), the fiber cellulose content
2 (measured between 75.9 and 86.2%) is large enough to confer high mechanical properties to
3 flax fibers. Thus, if basal values of tensile parameters would be insured by the high rate of
4 cellulose, the variations between minimal and maximal values were mainly due to the
5 structuring and detailed organization of the cell walls. This hypothesis is reinforced by the
6 importance of the EOH/EH ratio which quantifies the structuring components part into the S2
7 layer. Moreover, improvements into mechanical properties and Young's Modulus
8 accommodation noticed after cyclic loadings (Placet, 2009) showed that micro-fibrils
9 reorientation and changes into cell wall structuring have a real influence on the fiber mechanical
10 properties.

11 Regarding our previous preliminary data on Hermes and Oliver (Alix et al., 2009b), which dealt
12 with the impact of the presence of pectic acid - and more especially of homogalacturonan - in
13 EOH, we looked for any correlation between the content of the uronic acids (UA) and the
14 mechanical properties. In the present study, a positive correlation has been found, - especially
15 in EH - between the UA percentage (relative to the mass of polysaccharides) and the strain at
16 break. The more important the UA quantity in the matrix, the higher the sliding between micro-
17 fibrils during the tensile loading. When expressed per g of fibers, the content of UA was not
18 related to strain any more. On the other hand, UA' in EOH was positively related with strength
19 and, more interestingly, with E, while UA' in EH was negatively related with E. As evidenced in
20 figure 5, the ratio UA' EOH/EH³ showed the highest positive correlation with the tensile module
21 ($r^2 = 0.85$). If we omitted the not completely mature Everest 2005 fiber (Pillin et al., 2011), the r^2
22 value would reach the extreme value of 0.96.

23 It was also worth observing that MFA was highly negatively related to this ratio.

24 To sum up, the most remarkable impact of the chemical composition on both the tensile
25 modulus and the MFA dealt with the presence of pectins in EOH. We had previously
26 hypothesized that HGA would reinforce the interface between the cellulose microfibrils and the
27 RG-I matrix (Alix et al., 2009b). The present data indicate that pectic acids also play a role in the
28 orientation of the micro-fibrils at the time of their synthesis, as suggested by Roland et al.
29 (Roland et al., 1995).

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Finally, an interesting relationship was found between the MFA and the flax fiber mechanical properties, as it exists for wood but within a much wider range of MFA values (Salmén, 2004). A strong negative correlation exists between the MFA and the flax fibers Young's modulus ($r^2 = -0.75$). This correlation is moderate with the tensile strength at break ($r^2 = -0.37$) and the strain at break ($r^2 = 0.23$).

As explained in the experimental section, micro-fibrillar angles have been obtained on non-solicited fiber bundles whereas the Young's modulus has been calculated on the second part of the stress-strain curve of elementary fibers. This point could be questionable, but the determination of the stiffness in the first part of the stress-strain curve has little meaning due to the progressive loading of the micro fibrils occurring at the beginning of the test; in this case, the values that were obtained would not be representative of the real properties of the flax fibers.

In order to extend the measurement range, values from elementary hemp fibers have been plotted (Placet et al., 2011). These results show the importance of the MFA on the mechanical properties, and especially on the Young's modulus. The correlation is lower with the strength at break. We can suppose that, in the case of an important MFA, the reorientation at the beginning of the tensile loading is more important and longer, and could affect the cell wall structuring as well as have a negative effect on the stiffness and the strength of the fibers. Indeed, whatever their MFA, the initial micro-fibril conformations are similar, and the elementary fibers have to exhibit closely related mechanical properties, at equivalent cellulose contents.

There is no correlation between the MFA and the elementary fibers strain at break. It is indeed possible to observe some variety with low MFA and important strains (Ariane variety), whereas the contrary could be expected. Intrinsic cell wall parameters, which are dependent upon the structuring of the polysaccharidic network, may or may not, depending on this conformation, be thought to facilitate the strain of the fibers. This is reinforced by the good correlation existing between the UA in EH and the strain at break (0.79), which shows that matrix pectins rate is directly linked to the strain of the elementary fibers.

4 Conclusions

For the first time concerning plant cellulosic fibers, it was shown that the lower the MFA, the higher the Young's modulus. Moreover, this work tends to indicate the importance of the ratio between the amount of coating polymers and that of the matrix pectin on tensile behavior.

Importantly, the content of uronic acids seems to be positively correlated with the Young's modulus, highlighting their structural role in the tensile properties of the flax cell walls. Due to their negative correlation with the MFA, we hypothesize that pectic acids may influence the micro-fibrillar orientation when they are secreted in the secondary wall.

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36 37 38 39 40 41 42 **Figures captions**

43
44 **Figure 1.** Schematic representation of flax fiber showing helix arrangement of cellulose fibrils
45 (a) and stress-strain curve of an elementary flax fiber (b). Adapted from Hearle (Hearle, 1963)
46 and Baley (Baley, 2002).

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48 **Figure 2.** X-ray diffraction method: (a) example of optimal 002 circle, (b) curve fitting:
49 Experimental signal / model, (c) One image taken before data acquisition at one spot along the
50 fiber bundle. The circle represents the diameter of the x-ray beam.

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52 **Figure 3.** Relative polymer distribution in flax fibers (the dark bar represents the textile flax and
53 the clear ones the oleaginous varieties)

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55 **Figure 4.** Schematic representation of biochemical arrangement of the flax fiber S2 layer

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59 **Figure 5.** Correlations between the flax fibers Young's Modulus and the UA EOH / UA EH ratio.

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Tables captions

Table 1. Flax varieties used for the study.

Table 2. Mechanical properties of elementary plant fibers.

Table 3. MFA of plant fibers obtained by using X-ray diffraction.

Table 4. Cell-wall composition of fibers. 1- mg of UA per mg of extract. 2- mg UA per g of fiber.
3- the ratio was between the UA expressed in mg per g of fiber.

Table 5. Correlations between the biochemical composition or the MFA and the mechanical properties or MFA. The r^2 values were calculated considering the hypothesis of a linear correlation. The sign (-) corresponded to a negative slope.

1- mg of UA per mg of extract. 2- the ratio was between the UA expressed in mg per g of fiber.

Table 1. Flax varieties used for the study.

Flax variety	Type of flax	Culture year	Culture Area
Hermes	Textile	2003	France (Normandy)
Ariane	Textile	2002	France (Normandy)
Agatha	Textile	2003	France (Normandy)
Everest (E5)	Oleaginous	2005	France (Brittany)
Everest (E8)	Oleaginous	2008	France (Brittany)
Alaska	Oleaginous	2006	France (Brittany)
Hivernal	Oleaginous	2006	France (Brittany)
Oliver	Oleaginous	2003	France (Brittany)

Table 2. Mechanical properties of elementary plant fibers.

Fibers	Number of fibers	Average diameter (μm)	Young Modulus (GPa)	Strength at break (MPa)	Elongation at break (%)
Hermes 2003	37	19.6 ± 6.7	68.2 ± 35.8	1454 ± 835	2.3 ± 0.6
Ariane 2002	77	23.0 ± 5.7	54.1 ± 15.1	1339 ± 486	3.3 ± 0.8
Agatha 2003	45	21.3 ± 6.3	57.0 ± 29.0	865 ± 413	1.8 ± 0.7
Everest 2005	9	16.9 ± 4.9	41 ± 12.5	663 ± 307	1.8 ± 0.4
Everest 2008	30	15.4 ± 5.1	75 ± 21.6	1232 ± 554	2.1 ± 0.8
Alaska 2006	20	15.3 ± 5.4	46.3 ± 12.1	691 ± 253	1.8 ± 0.6
Hivernal 2006	23	12.9 ± 3.3	67.5 ± 23.7	1119 ± 490	1.9 ± 0.5
Oliver 2003	78	17.5 ± 3.6	47.2 ± 21.3	751 ± 414	1.7 ± 0.6
Hemp	50	25.4 ± 6.0	19.1 ± 11.3	685 ± 590	2.5 ± 1.1

Table 3 MFA of plant fibers obtained by using X-ray diffraction.

Fibers	MFA (°)
Hermes 2003	8.6 ± 0.2
Ariane 2002	9.1 ± 0.3
Agatha 2003	9.3 ± 0.4
Everest 2005	8.9 ± 0.1
Everest 2008	8.3 ± 0.2
Alaska 2006	9.5 ± 0.1
Hivernal 2006	8.8 ± 0.2
Oliver 2003	9.1 ± 0.2
Hemp	11.2 (Placet et al., 2011)

Table Cell-wall composition of fibers.

Fibers	Δm EH (%)	Δm EOH (%)	Δm EOH Δm EH	(%)	EA EH ¹ (mg/mg)	EA EOH ¹ (mg/mg)	UA' EH ² (mg/g)	UA' EOH ² (mg/g)	EA EOH EH ³
Hermes 2003	6.3	9.8	1.6	83.9	0.12	0.07	7.8	6.9	0.89
Ariane 2002	5.0	8.8	1.8	86.2	0.18	0.08	10.6	7.1	0.67
Agatha 2003	7.0	9.3	1.3	83.6	0.12	0.07	8.4	6.4	0.76
Everest 2005	9.7	10.5	1.1	79.8	0.11	0.06	10.5	6.1	0.58
Everest 2008	6.2	12.2	2.0	81.6	0.12	0.06	7.2	7.9	1.09
Hivernal 2006	10.5	13.6	1.3	75.9	0.08	0.05	8.3	7.2	0.87
Oliver 2003	10.8	6.0	0.6	83.2	0.09	0.07	9.3	4.1	0.44

¹ mg of UA per mg of extract.

² mg UA per g of fiber.

³ the ratio was between the UA expressed in mg per g of fiber.

Table 5 Correlations between the biochemical composition or the MFA and the mechanical properties or MFA.

	Young's Modulus (E)	Strength at break (σ)	Strain at break (ϵ)	MFA
EH (Δm %)	0.23 (-0,80, +0,57)	0.52 (-0,90, +0,29)	0.56 (-0,90, +0,29)	0.03 (-0,69, +0,72)
EOH (Δm %)	0.36 (-0,46, +0,85)	0.08 (-0,66, +0,74)	0.00 (-0,70, +0,71)	0.35 (-0,85, +0,47)
EOH/EH (%)	0.5 (-0,27, +0,90)	0.6 (-0,17, +0,92)	0.33 (-0,39, +0,87)	0.25 (-0,55, +0,81)
EA/EH (mg/mg) ¹	0.0 (-0,70, +0,71)	0.00 (-0,65, +0,75)	0.3 (-0,50, +0,83)	0.00 (-0,65, +0,75)
EA/EOH (mg/mg) ¹	0.0 (-0,70, +0,71)	0.23 (-0,80, +0,57)	0.56 (-0,90, +0,29)	0.0 (-0,66, +0,75)
UA' EH mg/g fiber	0.6 (-0,93, +0,12)	0.00 (-0,76, +0,64)	0.0 (-0,66, +0,75)	0.33 (-0,49, +0,84)
UA' EOH mg/g fiber	0.5 (-0,23, +0,91)	0.00 (-0,35, +0,88)	0.22 (-0,57, +0,80)	0.3 (-0,50, +0,83)
UA' EOH / UA' EH ²	0.35 (-0,36, +0,97)	0.38 (-0,44, +0,86)	0.02 (-0,69, +0,71)	0.53 (-0,90, +0,28)
MFA	0.05 (-0,95, -0,10)	0.3 (-0,85, +0,45)	0.23 (-0,80, +0,57)	

The r^2 values were calculated considering the hypothesis of a linear correlation. The sign (-) corresponded to a negative slope. Values in brackets are the 95% confidence intervals.

¹ mg of UA per mg of extract.

² the ratio was between the UA expressed in mg per g of fiber.

Figure

Figure Schematic representation of flax fiber showing helix arrangement of cellulose fibrils (a) and stress-strain curve of an elementary flax fiber (b). Adapted from Hearle (Hearle, 1963) and Baley (Baley, 2002)

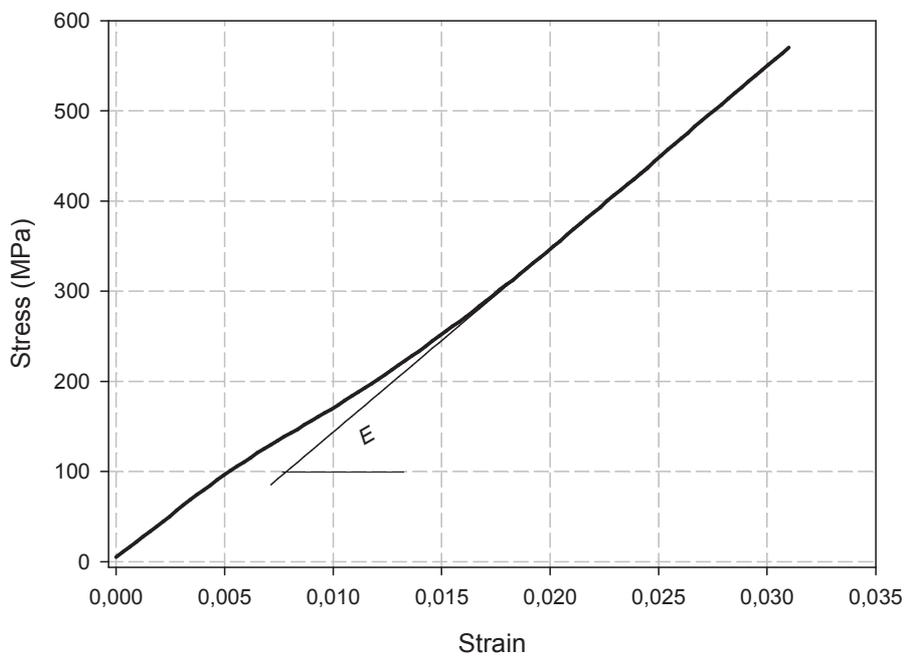
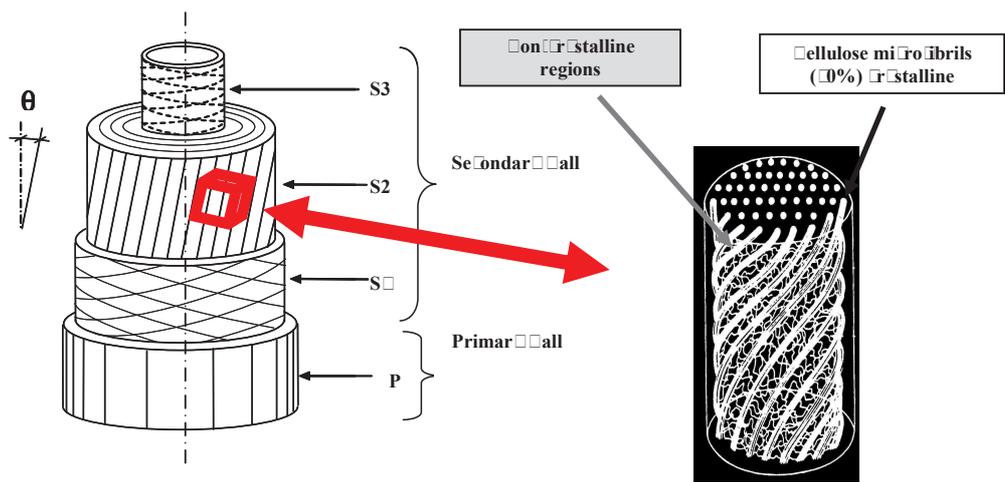


Figure 2. X-ray diffraction method: (a) example of optimal 002 circle, (b) curve fitting: Experimental signal / model, (c) One image taken before data acquisition at one spot along the fiber bundle. The circle represents the diameter of the x-ray beam.

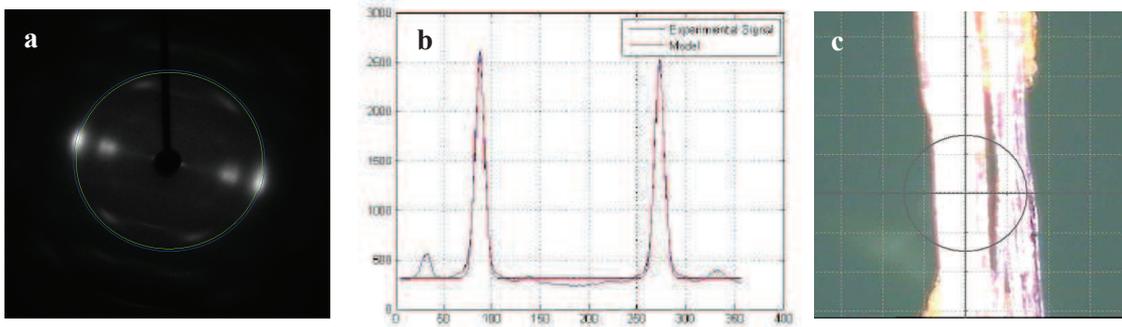


Figure 1 Relative polymer distribution in flax fibers (the dark bar represents the textile flax and the clear ones the oleaginous varieties)

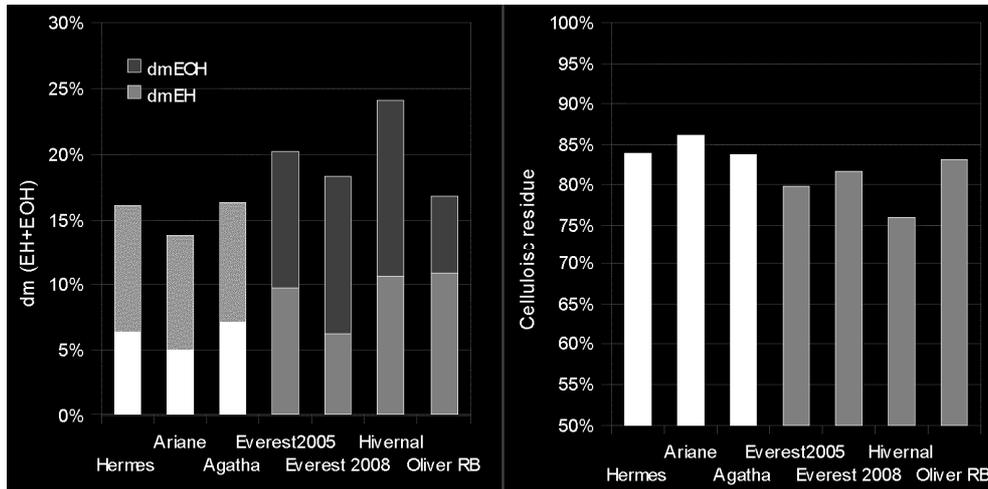


Figure □ Schematic representation of biochemical arrangement of the flax fiber S2 layer

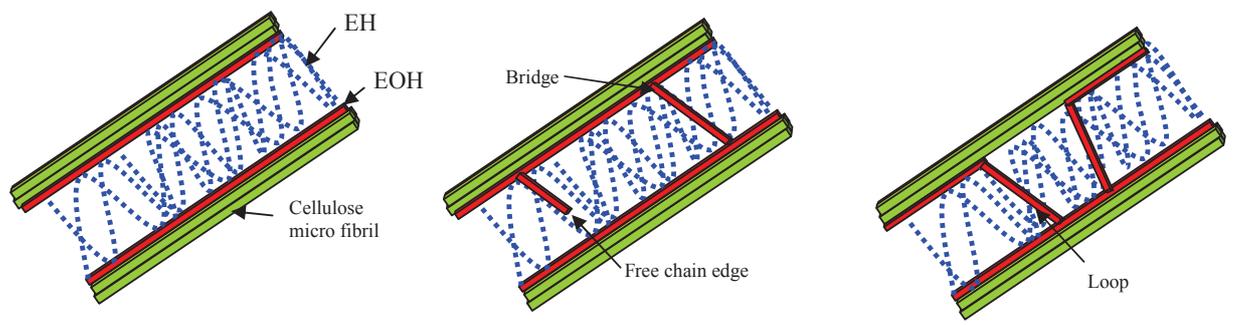


Figure □ Correlations between the flax fibers Young's Modulus and the UA EOH /

UA EH ratio. $r^2=0.85$

